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(54) **Polyol and utilization thereof.**

(57) The present invention relates to a polyol, polyurethane resin, rigid polyurethane foam, preparation process thereof and a preparation process of a rigid polyurethane foam composite.

The polyol used in the present invention comprises a phenol resin base polyol mixed with an aminophenol base polyol or a polyphenylpolyxylylenepolyamine base polyol or a polymethylenepolyphenylpolyamine base polyol.

The above polyurethane resin, foam and composite have resistance to dissolution in a hydrochlorofluorocarbons and a hydrofluorocarbons which are foaming agents having very low public hazard.

The above-mentioned foams have excellent physical properties equivalent to those of conventional polyurethane foams obtained by using chlorofluorocarbons, and hence are very useful as a thermal insulation material or a thermal insulation structure for refrigerators, freezers, insulation panels, ships or vehicles.

EP 0 483 431 A1

The present invention relates to a polyol, polyurethane resin, rigid polyurethane foam, preparation process thereof and a composite of said rigid polyurethane foam.

More particularly, the polyol used in the present invention comprising a phenyl resin base polyol mixed with an aminophenol base polyol or polyphenylpolyxylenepolyamine base polyol or poly-methylenepolyphenylpolyamine base polyol is a raw material for preparing polyurethane resin having resistance to dissolving in hydrochlorofluorocarbons (hereinafter abbreviated as HCFC) and hydrofluorocarbons (hereinafter abbreviated as HFC) which are foaming agents causing very low public hazards. The polyol can provide rigid polyurethane foam and its composite by using the above foaming agents

The rigid polyurethane foam among above products obtained specially has excellent properties equivalent to those of conventional polyurethane foams obtained by the use of chlorofluorocarbons (hereinafter abbreviated as CFC) as foaming agents. Hence, the rigid polyurethane foam of the present invention is extremely useful for the insulating materials or the insulating structural materials of electric refrigerators, freezing ware houses, insulation panels, ships and vehicles.

#### (b) Description of the Prior Art

Rigid polyurethane foam has excellent heat insulation property and low temperature dimensional stability and thus various composites prepared therefrom are widely used for refrigerators, freezing ware houses, building wall faces, ceilings, heat insulation and structural materials for ships and vehicles, and the heat insulating and protective covers of instruments.

Further, composites containing the rigid polyurethane foam formed on a sheet of face material or in a cavity surrounded by a plurality of face material have already been broadly manufactured by a batch process or a continuous process.

In the present manufacturing process of polyurethane foams, particularly CFC such as CFC-11 and CFC-12 are generally used as foaming agents. These compounds have recently recognized as materials for causing environmental destruction such as disruption of ozone layer or enhancement of green house effect. Accordingly, restriction has recently been imposed upon the manufacture and use of these compounds.

At the same time, HCFC such as 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), 1,1-dichloro-1-fluoroethane (HCFC-141b) 1-chloro-1,1-difluoroethane (HCFC-142b), 1-chloro-1,1-difluoromethane (HCFC-22) and additionally HFC such as 1,1,1,2-tetrafluoroethane (HFC-134a) and 1,1-difluoroethane (HFC-152a) which cause much less environment destruction have been focused attention as substitutes for CFC-11 and CFC-12. However, it was found that HCFC and HFC have higher dissolving power to polyurethane resin as compared with CFC, and hence have disadvantages of severely deteriorating the properties of resulting polyurethane foams, for example, reduction of closed cell content and foam strength. Particularly it has been found by the present inventors that in the manufacture of rigid polyurethane foams, HCFC and HFC dissolve cell wall of closed cells in the course of foaming and drastically lowers heat insulation effect which is a characteristic property of rigid polyurethane foams.

Consequently, a novel polyurethane resin has been desired strongly to dissolve above problems. The conventional polyoxyalkylene polyol used for the raw material of polyurethane resin decreases viscosity according to increase in the amount of alkylene oxide added. As a result, operations in polyurethane foam production can be conducted with ease. It has been found that excess addition of alkylene oxide leads to dissolution of polyurethane resin into HCFC and HFC, and tends to made application of these foaming agents substantially impossible. On the other hand, when the amount of alkylene oxide added is reduced, it has been certified that a resistance to dissolving in HCFC and HFC is improved slightly, but the polyol becomes solid or extremely viscous and solubility between each raw material decreases and it is very difficult to handle, successively satisfactory product cannot be obtained.

Specially, in the production of rigid polyurethane foam, viscosity of polyol and solubility between polyol, foaming agent and organic polyisocyanate are necessary, and polyol which has a viscosity suitable for foaming operation and is excellent in the mixing and dispersing ability in HCFC and HFC has never been found.

Inventions of Japanese TOKKAI-SHO 57-151613(1982) and TOKKAI-SHO 57-151614(1982) disclose a method of blending low molecular weight polyol in order to decrease the viscosity of mixture of amine base polyol and aromatic base polyester polyol (alkylene oxide was not added).

TOKKAI-Sho 51-105394 (1976) disclose mixed polyol having hydroxyl value of 200~500 mgKOH/g comprising novolak base polyol, aromatic amine base polyol and aliphatic polyol. TOKKAI-Sho 63-264616 and TOKKAI-Hei 1-135824 disclose mixed polyol comprising novolak resin base polyol having hydroxyl

value of 50–350 mgKOH/g, polyetherpolyol and/or polyesterpolyol. But these inventions have not indicated the polyols of the present invention and the rigid polyurethane foam produced from their polyol and HCFC or HFC.

The present invention relates to a polyol, polyurethane resin, rigid polyurethane foam, preparation process thereof and a preparation process of a rigid polyurethane foam composite.

The polyol used in the present invention comprises a phenol resin base polyol mixed with an aminophenol base polyol or a polyphenylpolyxylylenepolyamine base polyol or a polymethylenepolyphenylpolyamine base polyol.

The above polyurethane resin, foam and composite have resistance to dissolution in a hydrochlorofluorocarbons and a hydrofluorocarbons which are foaming agents having very low public hazard.

The above-mentioned foams have excellent physical properties equivalent to those of conventional polyurethane foams obtained by using chlorofluorocarbons, and hence are very useful as a thermal insulation material or a thermal insulation structure for refrigerators, freezers, insulation panels, ships or vehicles.

The primary object of the present invention is, particularly in the production of a rigid polyurethane foam, to provide a polyol which gives equivalent operation efficiency in polyurethane foaming operation and equivalent resultant foam properties to those of using conventional CFC, even though HCFC and/or HFC having very low hazards are used.

As a result of an intensive investigation in order to achieve the above object, the present inventors have completed the present invention.

That is, the aspect of the present invention is illustrated by the following (1) to (6).

(1) Polyol(D) comprising phenol resin base polyol(A) and aminophenol base polyol (B) in a ratio (A)/(B) of from 0.25 to 4.0 by weight, said polyol (D) having a hydroxyl value of from 180 to 700 mgKOH/g.

(2) Polyol(E) comprising phenol resin base polyol(A) and polyphenylpolyxylylenepolyamine base polyol-(C) in a (A)/(C) ratio of from 0.25 to 4.0 by weight, said polyol(E) having a hydroxyl value of from 180 to 700 mgKOH/g.

(3) A polyurethane resin obtained by the reaction of a polyol with an organic polyisocyanate wherein a portion or the whole of said polyol is the polyol(D) described in (1) or the polyol(E) described in (2).

(4) A rigid polyurethane foam obtained by the reaction of an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator and other additives, said polyol comprising the polyol(D) described in (1), the polyol(E) described in (2), or a polyol (G) comprising a phenol resin base polyol (A) and polyphenylpolymethylenepolyamine base polyol(F), said foaming agent comprising a compound or a mixture thereof selected from the group consisting of a HCFC and HFC, said foaming agent additionally comprising an auxiliary foaming agent, if desired.

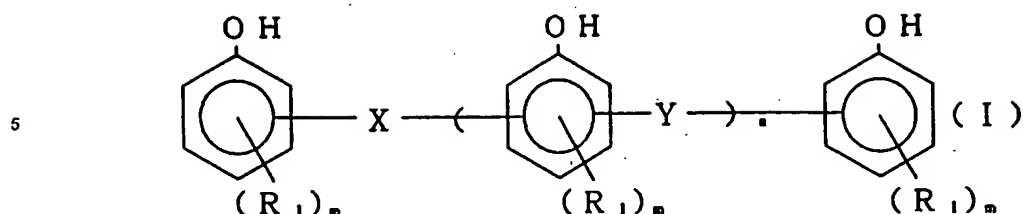
(5) A preparation process of the rigid polyurethane foam described in (4).

(6) A preparation process of a rigid polyurethane foam composite by reacting an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator and other additives to form a rigid polyurethane foam on a face material or in a cavity surrounded by a plurality of the face material, said polyol comprising polyol(D) described in (1), polyol(E) described in (2), or a polyol (G) comprising phenol resin base polyol (A) and polyphenylpolymethylenepolyamine base polyol(F), said foaming agent comprising a compound or a mixture thereof selected from the group consisting of a HCFC and a HFC, said foaming agent additionally comprising an auxiliary foaming agent, if desired.

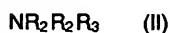
The polyol for use in the present invention is the above polyol(D), polyol(E) and polyol(G).

Polyol(D) used in the present invention comprises its component, phenol resin base polyol (A) and another component, aminophenol base polyol (B).

Phenol resin base polyol(A) used in the invention comprises polyol(a) and polyol(b) or polyol (a) and polyol(c); said polyol(a) having a hydroxyl value of from 140 to 350 mgKOH/g and being prepared by the addition of from 1.0 to 4.5 moles of an alkylene oxide to one equivalent of hydroxyl of a phenol resin or a mixture thereof having a number average molecular weight (hereinafter abbreviated as (Mn)) of from 650 to 1400, an average functionality of from 3 to 8 and the formula (I):



10 wherein  $R_1$  is a hydrogen atom, alkyl having from 1 to 9 carbon atoms, halogen atom selected from chlorine, bromine and fluorine, or hydroxyl,  $m$  is an integer of from 1 to 3,  $n$  is an integer of from 1 to 6, and  $X$  and  $Y$  are same or different divalent group selected from the group consisting of an alkylene having from 1 to 10 carbon atoms, xylene, oxy, thio and sulfonyl or bonded group of the above-mentioned groups; said polyol(b) having a hydroxyl value of 240 to 800 mgKOH/g and being obtained by adding from 0.5 to 3.0 moles of an alkylene oxide to one equivalent of active hydrogen in an alkanolamine series compound or a mixture thereof having the formula (II):



20 wherein  $R_2$  and  $R_3$  are respectively a hydrogen atom, hydroxyethyl or hydroxyisopropyl,  $R_2$  and  $R_3$  are same or different and excluding the case wherein both  $R_2$  and  $R_3$  are hydrogen atoms; said polyol(c) having a hydroxyl value of 130 to 750 mgKOH/g and being obtained by the addition of from 0.8 to 6.5 moles of an alkylene oxide to one equivalent of hydroxyl in an active hydrogen containing compound which is an aliphatic polyhydroxy compound having functionality of from 2 to 8 or a mixture thereof.

25 The suitable phenol resin for use in the invention includes, for example, reaction products of phenols such as phenol, cresol, butylphenol, nonylphenol, chlorophenol, resorcinol, hydroquinone, catechol, guaiacol, bisphenol A or bisphenol S with aldehydes such as formaldehyde or acetaldehyde,  $\alpha$ ,  $\alpha'$ -dimethoxyxylene,  $\alpha$ ,  $\alpha'$ -dichloroxylene or sulfur. The reaction is carried out by known methods.

30 Preferred phenol resin is a novolak resin which has the formula (I) wherein  $R_1$  is a hydrogen atom and both  $X$  and  $Y$  are methylene, and has (Mn) of 650 to 900, average functionality of 3 to 8, and a softening point of 75 to 120 °C.

The alkylene oxide used for the present invention includes, for example ethylene oxide, propylene oxide and butylene oxide. The alkylene oxide may be used singly or in combination.

35 It was found that when mole numbers of alkylene oxide addition are increased, solubility resistance to HCFC or HFC is generally decreased.

When (Mn) of the phenol resin is less than 650, any of the polyurethane resin derived from the reaction with organic polyisocyanate has a tendency to dissolve in HCFC and HFC.

40 On the other hand, (Mn) of the phenol resin exceeding 1400 leads to high viscosity in any mixing ratio, poor dispersibility in HCFC and HFC, inferior operation efficiency in reaction, with organic polyisocyanate.

The suitable polyol (a) for use in the invention is obtained by the addition of 1.0 to 4.5 moles of alkylene oxide to 1 equivalent of the hydroxyl group in the phenol resin. Alkylene oxide of less than 1.0 mole, that is, much amount of phenolic hydroxyl group remained causes unfavorable reduction of physical properties in the resulting polyurethane foam. On the other hand, alkylene oxide addition exceeding 4.5 mole eliminates resistnace to HCFC or HFC of resulting polyurethane resin, although viscosity is reduced and dispersibility in HCFC and HFC becomes better.

45 When the phenol resin has an average functionality of less than 3, the resulting polyurethane resin made from (a) and (b) or (a) and (c) decreases resistance to HCFC and HFC. On the other hand, average functionality exceeding 8 leads to a disadvantage of rendering the polyurethane resin brittle.

50 The alkanolamine for use in the invention includes, for example, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine and triisopropanolamine.

The suitable polyol (b) used in the invention is obtained by the addition of 0.5 to 3.0 moles of alkylene oxide to 1 equivalent of active hydrogen in the alkanolamine.

55 When the amount of alkylene oxide is less than 0.5 mole per equivalent of active hydrogen of alkanolamine, crosslinking activity of alkanolamine remains and hence deteriorates physical properties of resulting polyurethane foam. The amount of alkylene oxide exceeding 3.0 moles also decreases foam properties and the resulting polyurethane foam cannot be practically used.

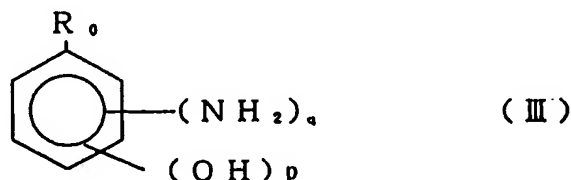
The polyols (a) and (b) used in the invention are preferably used in a mixing ratio (a)/(b) of 0.25 to 4.0 by weight. The mixing ratio exceeding 4.0 causes high viscosity and poor dispersibility and dissolving in HCFC and HFC and also leads to unfavorable operation problems on the preparation of polyurethane resin. On the other hand, the mixing ratio less than 0.25 is unsuitable because of inferior properties of resulting polyurethane foams and a deterioration of resistance to dissolving in HCFC or HFC.

The suitable aliphatic polyhydroxy compounds used for the present invention is a single compound or a mixture of two or more compounds selected from the group consisting of a glycols, polyhydric alcohols and a polysaccharides having 2 to 8 functionality. Exemplary aliphatic polyhydroxy compounds includes glycols such as ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, butanediol, neopentyl glycol, cyclohexane dimethanol and cyclohexane tetramethanol; polyhydric alcohols such as glycerol, trimethylolethane, trimethylolpropane, and pentaerythritol; and polysaccharides such as methylglucoside, sorbitol, mannitol, dulcitol and sucrose.

Preferred mole numbers of alkylene oxide addition is from 0.8 to 6.5 moles per equivalent of the hydroxyl in the aliphatic polyhydroxy compound. Alkylene oxide addition of less than 0.8 mole makes resultant polyurethane foam brittle. On the other hand, addition exceeding 6.5 moles lowers resistance to HCFC and HFC of the polyurethane resin obtained.

The polyols (a) and (c) which are initiated with the phenol resin and aliphatic polyhydroxy compound, respectively, are preferably mixed in the ratio (a)/(c) of 0.1 to 4.0 by weight. The mixing ratio less than 0.1 reduces resistance to HCFC or HFC of polyurethane resin prepared by reacting in the presence of a catalyst. On the other hand, the mixing ratio exceeding 4.0 leads to a disadvantage of poor operation efficiency due to too high viscosity in the preparation of polyurethane resin.

Aminophenol base polyol (B) comprises polyol(d) having a hydroxyl value of from 150 to 700 mgKOH/g and polyol(b) or polyol (d) and polyol(c) described in the phenol resin base polyol (A), said polyol(d) being obtained by adding from 1.0 to 9.0 moles of an alkylene oxide to one equivalent of active hydrogen in an aminophenol series compounds or a mixture thereof having a (Mn) of from 100 to 200, average functionality of from 3 to 6, and the formula (III):



wherein  $\text{R}_0$  is a hydrogen atom, aliphatic hydrocarbon group having from 1 to 5 carbon atoms, or alicyclic hydrocarbon,  $q$  is an integer of from 1 to 2, and  $p$  is an integer of from 1 to 2.

Exemplary suitable aminophenol compound includes aminophenol, aminocresol, aminoethylphenol, aminobutylphenol, aminoresorcinol, aminopyrocatechol, aminohydroquinone, aminohomocatechol, aminocresorcinol, aminoocrcinol, diaminophenol, diaminocaresol.

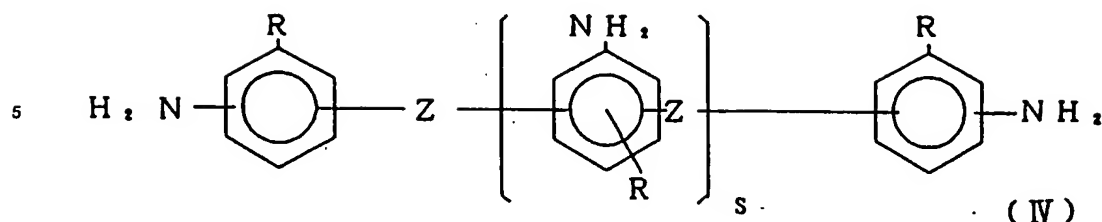
Aminophenol base polyol(B) comprises polyol(d) and polyol(b) or polyol (d) and polyol(c) in a (d)/(b) ratio of from 0.25 to 4.0 by weight and a (d)/(c) ratio of from 0.1 to 4.0 by weight. The reason for the selection of these mixing ratios is the same as (a)/(b) and (a)/(c) in the case of phenol resin base polyol(A).

Polyol(D) comprises phenol resin base polyol(A) and aminophenol base polyol(B) in a (A)/(B) ratio of from 0.25 to 4.0 by weight and has a hydroxyl value of from 180 to 700 mgKOH/g.

Even though polyol(A) is used singly, the rigid polyurethane foam obtained by using HCFC and/or HFC as foaming agents exhibits relatively good physical properties. When polyol(A) is used in combination with polyol(B), foam properties such as heat conductivity, compressive strength, and low temperature dimensional stability can be further improved. The (A)/(B) ratio deviated from the range of from 0.25 to 4.0 leads to inferior properties of the foam.

Another polyol (E) used of the present invention comprises its component, afore-mentioned phenol resin base polyol (A) and other component, polyphenylpolyxylylenepolyamine base polyol (C).

Polyphenylpolyxylylenepolyamine base polyol(C) used in the present invention comprises a polyol(e) having a hydroxyl value of from 150 to 700 mgKOH/g and polyol(b) or polyol (b) and polyol(c) described above, said polyol(e) being obtained by adding from 1.0 to 9.0 moles of an alkylene oxide to one equivalent of active hydrogen in a polyphenylpolyxylylenepolyamine series compound or a mixture thereof having the formula (IV):



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1 to 10 carbon atoms, or alicyclic hydrocarbon, Z is xylylene group, and s is an integer of from 0 to 10.

Above polyphenylpolyxylylenepolyamine series compound for use in the invention includes, for example,  $\alpha$ ,  $\alpha'$ -bis (4-aminophenyl)xylylene, polyphenylpolyxylylenepolyamine, mixture thereof derivatives, isomer and oligomer of these compounds.

15

When the amount of alkylene oxide is less than 1.0 mol per equivalent of the amino group, that is, many amino groups are remained, control of foaming reaction becomes difficult and the resulting polyurethane foam unfavorably deteriorates physical properties. On the other hand, alkylene oxide addition exceeding 9.0 moles leads to inferior physical properties, although viscosity is reduced and dispersing ability into HCFC and HFC becomes better.

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The alkanolamine which can be used has been described above.

The polyol(b) used in the invention is obtained by the addition of 0.5 to 3.0 moles of alkylene oxide to 1 equivalent of active hydrogen in the alkanolamine.

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When the amount of alkylene oxide is less than 0.5 mole per equivalent of active hydrogen of alkanolamine, crosslinking activity of alkanolamine remains and hence deteriorates physical properties of resulting polyurethane foam. The amount of alkylene oxide exceeding 3.0 moles also decreases foam properties even in a polyol mixing ratio (e)/(b) of above 4.0 and the resulting polyurethane foam cannot be practically used.

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The polyol (e) and (b) for use in the invention are preferably used in a mixing ratio (e)/(b) of 0.25 to 4.0 by weight. The mixing ratio exceeding 4.0 causes high viscosity and poor dispersibility in HCFC and HFC and also leads to unfavorable operation problems on the preparation of polyurethane resin. On the other hand, the mixing ratio less than 0.25 is unsuitable because of inferior properties of resulting polyurethane foams.

The aliphatic polyhydroxy compound which can be used has been described above.

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The preferred amount of an alkylene oxide added to the aliphatic polyhydroxy compound is from 0.5 to 6.5 moles per equivalent of hydroxyl group in the aliphatic polyhydroxy compound. Addition less than 0.5 mole makes resulting polyurethane foam brittle. On the other hand, the amount exceeding 6.5 moles decreases resistance of resulting polyurethane resin to dissolution in HCFC and HFC. Polyphenylpolyxylylenepolyamine initiated polyol(e) and aliphatic polyhydroxy compound initiated polyol(c) are preferably mixed in a (e)/(c) ratio of from 0.1 to 4.0 by weight. The ratio less than 0.1 lowers resistance to dissolving in HCFC and HFC of polyurethane resin prepared in the presence of a catalyst. On the other hand, the ratio exceeding 4.0 causes too high viscosity of resulting mixture and hence has a disadvantage of poor operation efficiency in the production of polyurethane resin.

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Polyol(E) is obtained by mixing polyol(A) and polyol(C) in a (A)/(C) ratio of from 0.25 to 4.0 by weight and has a hydroxyl value of from 180 to 700 mgKOH/g.

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Although polyol(A) is used singly, the foam obtained by using HCFC and/or HFC as foaming agents exhibits relatively good physical properties. When polyol(A) is used in combination with polyol(C), much better results can be obtained on the foam properties such as heat conductivity, compressive strength and dimensional stability. However, the ratio (A)/(C) deviated from the range of from 0.25 to 4.0 leads to inferior properties of the polyurethane foam obtained by using HCFC and/or HFC as foaming agents. Consequently, preferred (A)/(C) ratio is in the range of from 0.25 to 4.0.

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Polyol (G) used for preparing rigid polyurethane foam and composite thereof in the present invention comprises its component, afore-mentioned phenol resin base polyol (A) and other component, polyphenylpolymethylenepolyamine base polyol (F).

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Polyol (F) comprises polyol(f) having hydroxyl value of 150~700 mgKOH/g, adding alkylene oxide of 1.0~9.0 mol per 1 equivalent of amino group in a polymethylenepolyphenylpolyamine and afore-mentioned polyol (b) or polyol (f) and polyol (c).

It is preferable that the mixing ratio in weight of polyol (f) and Polyol (b), i. e. (f)/(b) is 0.25~4.0, and that of polyol (f) and polyol (c), i. e. (f)/(c) is 0.1~4.0.

Polyol (G) is a mixture of polyol (A) and polyol (F) in which the mixing ratio in weight, i. e. (A)/(F) is 0.25~4.0 and hydroxyl value of the mixture is 180~700 mgKOH/g.

The relationship among mixing ratio of (f)/(b), (f)/(c) and (A)/(F), hydroxyl value of mixed polyols, physical properties of polyurethane, operation efficiency and effect of combination use of polyol (A) and polyol (F) is the same as that of polyol (D) and polyol (E).

The suitable polymethylenepolyphenylpolyamine for use in the present invention includes, for example, polymethylenepolyphenylpolyamine, which is used commonly as a raw material of poly-methylenepolyphenylpolyisocyanate, 4,4'-diaminodiphenylmethane which is separated from the poly-methylenepolyphenylpolyamine, its isomer or mixture of these isomers.

The catalyst which can be used in the present invention for the addition reaction of alkylene oxide to a single compound or mixture of phenol resin, alkanolamine series compound, aliphatic polyhydroxy compound, aminophenol series compound, polyphenylpoly xylylenepolyamine and polymethylenepolyphenylpolyamine as a starting materials is an amine catalyst and an alkali metal hydroxide catalyst.

The amine catalyst is represented by the formula (V) or the formula (VI)



wherein  $\text{R}_4$  is a hydrogen atom or a group selected from a group consisting of alkyl having from 1 to 6 carbon atoms, hydroxyethyl and hydroxyisopropyl,  $\text{R}_5$  is a hydrogen atom or a group selected from a group consisting of alkyl having from 1 to 4 carbon atoms hydroxyethyl and hydroxyisopropyl,  $t$  is an integer of from 1~6, but  $\text{R}_4$  and  $\text{R}_5$  cannot be hydrogen atoms at the same time in the formula (V)

Exemplary amine compound includes dibutylamine, ethylenediamine, tetramethylenediamine, monoethanolamine, diethanolamine, triethanolamine, isopropanolamine, triethylamine, tri-n-propylamine, di-n-propylamine, n-propylamine, n-amylamine, N,N-dimethylethanolamine, isobutylamine, isoamylamine and methyldiethylamine.

Alkali metal hydroxide can also be used as the catalyst for the above addition reaction. Representative examples of alkali metal hydroxide include lithium hydroxide, sodium hydroxide, potassium hydroxide, magnesium hydroxide, calcium hydroxide and barium hydroxide.

The above amine and alkali metal hydroxide catalysts can be used singly or in combination.

The amount of the above catalysts used for the invention is from 0.1 to 2.0 parts by weight per 100 parts by weight of the sum of above starting materials having active group such as amino group or active hydrogen. When alkali metal hydroxide catalyst is used, reacted solution is neutralized by acid solution such as phosphoric acid aqueous solution.

The polyol of the present invention can be prepared by charging in an autoclave, the catalyst and a single starting material or a mixture thereof selected from phenol resin, alkanolamine, aliphatic polyhydroxy compound, polyphenylpolyxylylenepolyamine series compound, and polymethylenepolyphenylpolyamine and then gradually feeding an alkylene oxide to conduct addition reaction. Preferred reaction temperature is 90 to 130 °C. The temperature of lower than 90 °C is difficult to progress the reaction. On the other hand, the temperature exceeding 130 °C is liable to cause side reactions. When the above starting material is used singly, each polyol thus obtained can be subsequently blended in a prescribed amount.

The polyol in the present invention can be prepared by using a starting material singly or a mixture of it. In the case where the polyol prepared from the single material leads to high viscosity and poor operation efficiency, it is preferred to prepare the polyol by using a mixture of the starting material corresponding to each component of the desired polyol.

In the examples of the invention, each polyol (a), (b), (c), (d), (e) or (f) is separately synthesized by using the starting material singly and followed by mixing these polyols to prepare component polyols (A), (B), (C), and (F). Thereafter polyols (D), (E) and (G) of present invention are prepared by mixing the component polyols.

No particular restriction is imposed upon the organic polyisocyanate for use in the process of the invention.

Conventionally known organic polyisocyanates, for example, aromatic, aliphatic and alicyclic polyisocyanates and their modified products can be used. Exemplary polyisocyanate which is suitable for use includes phenylendiisocyanate, diphenylmethane diisocyanate, crude diphenylmethane diisocyanate, tolylene diisocyanate, crude tolylene diisocyanate, xylylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, hydrogenated diphenylmethane diisocyanate, hydrogenated tolylene diisocyanate, triphenylmethane triisocyanate, tolylene triisocyanate, polymethylenepolyphenylpolyisocyanate, modified

polyisocyanates such as carbodiimide modified diphenylmethane diisocyanate, and isocyanate terminated prepolymers which can be obtained by reacting the above polyisocyanate with the low molecular polyol or polymer polyol in a NCO/active hydrogen equivalent ratio of from 2 to 20 and have an isocyanate content of from 5 to 35% by weight.

5 These polyisocyanates can be used singly or in combination.

The equivalent ratio of the polyisocyanate to the hydroxyl group in the resin premix is in the range of from 0.8 to 5.0. The equivalent ratio exceeding 5.0 leads to unreacted polyisocyanate remained. On the other hand, the equivalent ratio less than 0.8 results in unreacted polyol remained. Hence the above range is preferable.

10 The foaming agent for use in the invention is HCFC and HFC.

Exemplary HCFC include 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123), 1,1-dichloro-1-fluoroethane (HCFC-141b) 1-chloro-1, 1-difluoroethane (HCFC-142b) and monochlorodifluoromethane (HCFC-22). Representative HFC includes 1,1,1,2-tetrafluoroethane (HFC-134a) and 1,1-difluoroethane (HFC-152a). These foaming agents can be used singly or in combination.

15 When necessary, water and/or low boiling point compound and other auxiliary foaming agent can be used in combination.

Water is usually used in an amount of from 0.5 to 5.0 parts by weight per 100 parts by weight of the resin premix. Exemplary low boiling point compound includes methylene chloride and other low boiling point hydrocarbons (boiling point is from 10 to 50 °C) and their mixture. Conventional CFC can also be used in combination.

20 The foaming catalyst which can be used for the rigid polyurethane foam, preparation of the invention includes, for example, amine catalyst such as triethylamine, tripropylamine, triisopropanolamine, tributylamine, trioctylamine, hexadecyldimethylamine, N-methylmorpholine, N-ethylmorpholine, N-octadecylmorpholine, monoethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N,N-dimethylethanolamine, diethylenetriamine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylpropylenediamine, N,N,N',N'-tetramethylbutanediamine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N,N',N'-tetramethylhexamethylenediamine, bis [2-(N,N-dimethylamino)ethyl] ether, N,N-dimethylbenzylamine, N,N-dimethylcyclohexylamine, N,N,N',N'', N''-pentamethyldiethylenetriamine, triethylenediamine, formic acid and other acid salts of triethylenediamine, oxyalkylene adducts of primary and secondary amines, aza ring compounds such as N,N-dialkylpiperazine, and various N,N',N''-trialkylaminoalkylhexahydrotriazines such as  $\beta$ -aminocarbonyl catalyst disclosed in Japanese TOKKO SHO 52-043517 (1977) and  $\beta$ -aminonitrile catalyst disclosed in Japanese TOKKO SHO 53-014279 (1978); and organometallic catalysts such as tin acetate, stannous octoate, stannous oleate, stannous laurate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin dichloride, lead octoate, lead naphthenate, nickel naphthenate and cobalt naphthenate.

35 These catalyst can be used singly or in combination. The amount of the catalyst for use is in the range of from 0.0001 to 10.0 parts by weight per 100 parts of the polyol.

The cell regulator for use in the present invention is a conventionally known organic silicone surfactant. Exemplary foam regulators include products of Nippon Unicar Co., Ltd. which are L-520, L-540, L-5340, L-5410, L-5420, L-5710 and -5720, products of Toray Silicone Co., Ltd. which are SH-190, SH-192, SH-193, SH-194, and SH-195, products of Shinetsu Silicone Co., Ltd. which are F-305, F-306, F-317, F-341 and F-345, and a product of Toshiba Silicone Co., Ltd. which is TFA-4200.

The amount of the cell regulator used is in the range of from 0.1 to 20 parts by weight per 100 parts by weight of the sum of the polyol and the organic polyisocyanate.

45 Flame retardants which can be used are tris(2-chloroethyl) phosphate, tris(dichloropropyl) phosphate, tris(dibromopropyl) phosphate, products of Daihachi Chemical Co., Ltd. which are CR-505 and CR-507, and a product of Akzo Japan Co., Ltd. which is Fyrol-6.

Other additives usually employed in polyurethane, for example, plasticizer, fillers, stabilizers, such as antioxidants, ultraviolet absorbers and colorants can also be added, if necessary.

50 In the case of preparing the polyurethane resin, the polyol, catalyst, stabilizer, organic polyisocyanate and other additives are mixed rapidly according to the formulation and poured into a mold, then are cured in room temperature. In the case of preparing the rigid polyurethane foam, the polyol, catalyst, cell regulator, flame retardant afore-mentioned foaming agent and other additives are mixed in a prescribed amount to foam a premix. Said polyol is that containing afore-mentioned polyol (D) or polyol (E) or polyol (G).

55 Using a polyurethane dispensing machine, the resin premix is rapidly and continuously mixed with the organic polyisocyanate at a constant ratio so as to obtain a NCO/active hydrogen equivalent ratio of from 0.8 to 5.0.



The mixture obtained is successively poured into a cavity or a mold. After pouring, liquid raw material of the rigid polyurethane foam is formed and cured in a serveral minutes.

The rigid polyurethane foam obtained in the present invention is used for the heat-insulation material or structural material of refrigerators, heat-insulating panels, ships and vehicles.

# Example

The present invention will hereinafter be illustrated further in detail by way of examples and comparative examples.

## [Polyol preparation]

### Reference Example 1

To a 21 autoclave, 500g of novolak resin #2000, a product of Mitsui Toatsu Chemicals, Inc. illustrated in Table 1, was charged. The internal atmosphere of the autoclave was replaced with nitrogen. The autoclave was then heated to 120°C, 2.3 g of triethylamine was added, and successively 274g of propylene oxide was gradually charged. After reacting for 3 hours unreacted propylene oxide was removed from the reaction system. Polyol (a-1) thus obtained was 720g and had a hydroxyl value of 339 mgKOH/g.

### Reference Example 2~9

Polyols (a-2~a-9) indicated in Table 2 were prepared by carrying out the same procedure as described in Reference Example 1, excepting the change of raw material formulation as indicated in Table 2.

Hydroxyl values of polyols prepared were indicated in Table 2.

### Reference Example 10~18

Polyols (b-1~b-7, c-1 and c-2) indicated in Table 3 were prepared by carrying out the same procedure as described in Reference Example 1, excepting the change of phenol resin in Reference Example 1 with triethanolamine, glycerol or trimethylolpropane in Reference Examples 10~18, and the change of raw material formulation as indicated in Table 3.

Hydroxyl values of these polyols were indicated in Table 3.

### Preparation of phenol resin base polyol (A)

#### Reference Examples 19~27

Polyol (A-1~A-9) was prepared by using the polyol (a), (b) and(c) prepared in Reference Examples 1~9 in Table 2 and Reference Examples 10~18 in Table 3.

Phenol resin base polyol (A-1~A-9) were prepared by the formulation indicated in Table 4. Hydroxyl values and viscosity values of these polyols were indicated in Table 4.

#### Reference Example 28~32

Polyols (d-1~d-5)indicated in Table 5 were prepared by carrying out the same procedure as discribed in Reference Example 1 excepting the change of phenol resin in Reference Example 1 with p-aminophenol and the change of raw material formulation as indicated in Table 5.

Hydroxyl values of these polyols were indicated in Table 5.

#### Reference Examples 33~37

Polyols (b-8~b-10, c-3 and c-4) indicated in Table 6 were prepared by carrying out the same procedure as described in Reference Example 1 excepting the change of phenol resin in Reference Example 1 with triethanolamine or glycerol and the change of raw material formulation as indicated in Table 6. Hydroxyl values of these polyols were indicated in Table 6.

Preparation of aminophenol base polyol (B)

Reference Examples 38~42

5 Aminophenol base polyols (B-1~B-5) were prepared by using the polyol (d), (b) and (c) prepared in Reference Examples 28~32 in Table 5 and Reference Examples 33~37 in Table 6. Aminophenol base polyols (B-1~B-5) were prepared by the formulation indicated in Table 7. Hydroxyl values of these polyols were indicated in Table 7.

10 Reference Example 43~48

Polyols (e-1~e-6) indicated in Table 8 were prepared by carrying out the procedure as described in Reference Example 1 excepting the change of phenol resin in Reference Example 1 with polyphenylpolyxylylenepolyamine, and the change of raw material formulation as indicated in Table 8.

15 Hydroxyl values of these polyols were indicated in Table 8.

Reference Example 49~54

20 Polyols (b-11~b-13 and c-5~c-7) indicated in Table 9 were prepared by carrying out the procedure as described in Reference Example 1 excepting the change of phenol resin in Reference Example 1 with triethanolamine or glycerol, and the change of raw material formulation as indicated in Table 9.

Hydroxyl values of these polyols were indicated in Table 9.

Preparation of polyphenylpolyxylylenepolyamine base polyol (C)

25

Reference Example 55~60

30 Polyphenylpolyxylylenepolyamine base polyols (C-1~C-6) were prepared by using the polyol (e), (b) and (c) prepared in Reference Examples 43~48 in Table 8 and Reference Examples 49~54 in Table 9, according to the formulation indicated in Table 10. Hydroxyl values and viscosity values of these polyols were indicated in Table 10.

Examples 1~11

35 Polyol (D) and (E) indicated in Examples 1~11 were prepared according to the formulation indicated in Table 11 by using phenol resin base polyols (A-1~A-9) indicated in Table 4, aminophenol base polyols (B-1~B-5) indicated in Table 7 and polyphenylpolyxylylenepolyamine base polyols (C-1~C-6) indicated in Table 10.

40 Hydroxyl values and viscosity values of these polyols obtained were indicated in Table 11.

Reference Example 61~66

45 Polyols (f-1~f-6) indicated in Table 12 were prepared by carrying out the same procedure as described in Reference Example 1, excepting the change of phenol resin in Reference Example 1 with polymethylenepolyphenylpolyamine. Hydroxyl values of these polyols were indicated in Table 12.

Reference Example 67~72

50 Polyols (b-14, b-15 and c-8~c-11) indicated in Table 13 were prepared by carrying out the same procedure as described in reference Example 1, excepting the change of phenol resin in Reference Example 1, with triethanolamine, glycerol or pentaerythritol, and the change of raw material formulation as indicated in Table 13. Hydroxyl values of these polyol were indicated in Table 13.

55

Reference Example 73-78

Polyphenylpolyxylenepolyamine base polyols (F) were prepared by using the polyols (f), (b) and (c) prepared in Reference Examples 61-66 indicated in Table 12 and Reference Examples 67-72 in Table 13, according to the formulation indicated in Table 14. Hydroxyl values and viscosity values of polyols thus obtained were indicated in Table 14.

Preparation of polymethylenepolyphenylpolyamine base polyol (F)

Reference Examples 79-84

Polyols (G-1~G-6) indicated in Table 15 were prepared according to the formulation indicated in Table 15 by using phenol resin base polyol (A-1~A-3, A-5, A-6 and A-9) indicated in Table 4 and polymethylenepolyphenylpolyamine base polyols (F-1~F-6). Hydroxyl values and viscosity values of these polyols obtained were indicated in Table 15.

Table 1  
Physical Properties of Novolak Resin and Phenol Base Resin

No.	Grade (•) (Product of MITSUI TOATSU CHEMICALS, INC.)	Number average molecular weight (Mn)	Average function- ality	Softening point (°C)
(1)	1000HS	867	7.70	115
(2)	2000	723	6.37	95
(3)	9000	654	5.62	93
(4)	Cresol/Novolak type	815	6.71	103
(5)	Bisphenol A/Novolphenol type	1032	5.18	121

Table 2

Reference Example No.	1	2	3	4	5	6	7	8	9
Polylol (a)	a-1	a-2	a-3	a-4	a-5	a-6	a-7	a-8	a-9
Phenol resin (No.: Table 1)	(g)	500 (2)	500 (3)	500 (4)	500 (5)	500 (1)	500 (2)	500 (2)	500 (3)
Propylene oxide	(g)	274	547	305	320	1231	821	300	547
Ethylene oxide	(g)								
Alkylenes oxide addition amount (mol/DEq.)	1.0	1.9	2.8	1.2	1.9	4.4	3.1	1.1	1.9
OH-value (eqOH/g)	339	250	204	285	182	153	198	320	250

Note: Eq: Equivalent  
OH-value: Hydroxyl value (JIS K 1507).

Table 3

Reference Example No.	10	11	12	13	14	15	16	17	18
Polylol (b) or (c)	b-1	b-2	b-3	b-4	b-5	b-6	b-7	c-1	c-2
Triethanolamine	(g)	500	500	500	500	500	250		
Glycerol	(g)							500	
Trimethylolpropane	(g)								500
Sucrose	(g)						250		
Propylene oxide	(g)	821	1348		706	1752	3530	832	4230
Ethylene oxide	(g)								
Alkylenes oxide addition amount (mol/DEq.)	0.5	2.1	0.6	0.5	1.1	2.9	4.1	0.8	6.2
OH-value (eqOH/g)	718	327	661	718	496	253	207	730	141

Table 4 Phenol Resin Base Polyol (A)

Reference Example No.	19	20	21	22	23	24	25	26	27
Mixed polyol (A)	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9
Polyol (a)	a-1	a-2	a-3	a-4	a-5	a-6	a-7	a-8	a-9
Polyol (b) or (c)	b-1	b-2	b-3	b-4	b-5	b-6	b-7	c-1	c-2
Mixing ratio (a)/(b) or (a)/(c) (weight)	1.0	0.43	1.0	1.0	0.67	1.5	1.0	1.5	3.0
OH-value (mgOH/g)	532	298	465	507	570	183	460	245	240
Viscosity (CP/25 °C)	19700	9670	13000	19700	30300	18900	6300	4900	9750

Note: OH-value: Hydroxyl value  
 Viscosity: JIS K 1557  
 Eq.: Equivalent

Table 5

Reference Example No.	28	29	30	31	32
Polyol (d)	d-1	d-2	d-3	d-4	d-5
P-methophenol (g)	327	327	218	218	373
Propylene oxide (g)	522	1044	1044	1568	
Ethylene oxide (g)					792
Alkyrene oxide addition amount (mol/DEq.)	1.0	2.0	3.0	4.5	2.0
OH-value (mgOH/g)	585	568	297	189	451

Table 6

Reference Example No.	33	34	35	36	37
Polyol (b) or (c)	c-3	c-4	b-8	b-9	b-10
Triethanolamine (g)			745	745	238
Glycerol (g)	82	276			82
Propylene oxide (g)	1131	654	453	870	1044
Ethylene oxide (g)					
Alkydene oxide addition amount (mol/OBEq.)	6.5	2.0	1.0	0.5	3.0
OH-value (mgOH/g)	137	382	713	521	251

Table 7 Aminoalcohol Base Polyol (B)

Reference Example No.	38	39	40	41	42
Mixed polyol (B)	B-1	B-2	B-3	B-4	B-5
Polyol (d)	d-1	d-2	d-3	d-4	d-5
Polyol (b) or (c)	c-3	c-4	b-8	b-9	b-10
Mixing ratio (d)/(b) or (d)/(c) (weight)	0.2	4.0	0.25	4.0	0.5
OH-value (mgOH/g)	214	370	625	255	320
Viscosity (CP/25 °C)	700	7200	890	4800	3300

Table 8

Reference Example No.	43	44	45	46	47	48
Polyl (e)	e-1	e-2	e-3	e-4	e-5	e-6
Polypbenylpolystylenespolysilane (e)	835	835	448	835	448	835
Propylene oxide	327	654	654	654	1473	
Ethylene oxide						497
Alkyrene oxide addition amount (mol/DEq.)	1.0	2.0	4.0	2.0	9.0	2.0
OH-value (mgKOH/g)	518	408	287	408	164	455

Note: Polypbenylpolystylenespolysilane: Adilix®, a product of Mitsui Toatsu Chemicals, Inc.

Table 9

Reference Example No.	49	50	51	52	53	54
Polyl (b) or (c)	c-5	c-6	b-11	c-7	b-12	b-13
Glycerol	92	450		278		
Triethanolamine			1043		1043	1043
Propylene oxide	1131	636	609	1044	609	609
Ethylene oxide						
Alkyrene oxide addition amount (mol/DEq.)	8.5	0.8	0.5	2.0	0.5	0.5
OH-value (mgKOH/g)	137	727	713	382	713	713

Table 10 Polyphenyl(polyvinyl)ene/polyamine base Polyol (C)

Reference Example No.	55	56	57	58	59	60
Mixed polyol (C)	C-1	C-2	C-3	C-4	C-5	C-6
Polyol (e)	e-1	e-2	e-3	e-4	e-5	e-6
Polyol (b) or (c)	c-5	c-6	b-11	c-7	b-12	b-13
Mixing ratio (e)/(b) or (e)/(c) (weight)	4.0	2.0	0.25	0.10	0.5	3.0
OH-value (mgKOH/g)	441	514	628	384	536	519
Viscosity (CP/25 °C)	22500	10700	3800	4200	7500	21500

Table 11 Polyol (D) and (E)

Example No.	1	2	3	4	5	6	7	8	9	10	11
Polyol No.	D-1	D-2	D-3	D-4	D-5	E-1	E-2	E-3	E-4	E-5	E-6
Polyol (A)	A-6	A-2	A-5	A-3	A-1	A-6	A-2	A-5	A-3	A-1	A-9
Polyol (B) or (C)	B-1	B-2	B-3	B-4	B-5	C-1	C-2	C-3	C-4	C-5	C-6
(A)/[(B)or(C)](weight)	0.25	2.0	4.0	0.5	4.0	4.0	2.0	0.25	3.0	1.0	0.33
OH-value (mgKOH/g)	210	320	420	325	480	243	370	577	445	535	450
Viscosity (CP/25°C)	1300	8800	14000	7000	12000	20000	10200	5800	8200	12500	15800



Table 12

Reference Example No.	61	62	63	64	65	66
Polyol (f)	f-1	f-2	f-3	f-4	f-5	f-6
Polyethylencopolyphenylpolyamides (g)	594	594	198	594	782	530
Propylene oxide	686	596	1044	348	484	
Ethylene oxide						590
Alkylenes oxide addition amount (mol/7HEq.)	2.0	2.0	9.0	1.0	1.0	2.53
OH-value (mgKOH/g)	520	520	180	715	723	516

Note: Polyethylencopolyphenylpolyamide MD4-150, a product of Mitsui Toatsu Chemicals, Inc.

Table 13

Reference Example No.	67	68	69	70	71	72
Polyol (b) or (c)	c-8	c-9	c-10	c-11	b-14	b-15
Glycerol (g)	363	276	92			
Pentaerythritol (g)				394		
Triethanolamine (g)						596
Propylene oxide (g)	696	1566	1131	1392	348	696
Ethylene oxide (g)						
Alkylenes oxide addition amount (mol/7HEq.)	1.0	3.0	6.5	3.0	0.5	1.0
OH-value (mgKOH/g)	630	274	140	253	723	525

Table 14 Polymethylolphenylpolyamine Base Polyol (F)

Reference Example No.	73	74	75	76	77	78
Mixed polyol (F)	F-1	F-2	F-3	F-4	F-5	F-6
Polyol (F)	f-1	f-2	f-3	f-4	f-5	f-6
Polyol (b) or (c)	c-8	c-9	c-10	c-11	b-14	b-15
Ratio (f)/(b) or (f)/(c) (weight)	4.0	3.0	0.1	1.0	4.0	1.0
OH-value (mgOH/g)	540	460	144	404	720	521
Viscosity (cP/25 °C)	5000	16500	11200	22500	23000	19400

Table 15 Polyol (G)

Reference Example No.	79	80	81	82	83	84
Polyol No.	G-1	G-2	G-3	G-4	G-5	G-6
Polyol (A)	A-6	A-2	A-5	A-3	A-1	A-8
Polyol (F)	F-1	F-2	F-3	F-4	F-5	F-6
(A) / (F) (weight)	4.0	0.67	0.25	1.0	0.25	3.0
OH-value (mgOH/g)	282	385	190	475	685	310
Viscosity (cP/25 °C)	18000	13100	14000	21000	22500	12500

## [Polyurethane resin Preparation](Examples 12~22)

Polyurethane resin was prepared by reacting 30.0 g of a polyol obtained in examples or comparative examples, an organic polyisocyanate MDI-CR (a product of Mitsui Toatsu Chemicals, Inc.) having NCO content of 31.0 %, and 0.10 g of amine catalyst Kaolizer No. 1 (Trademark, a product of Kao Co. Ltd.) at room temperature according to the formulation illustrated in Table 16.

CFC or HCFC absorption was measured on the polyurethane resin thus obtained. Results are illustrated in Table 16.

## [Rigid polyurethane foam preparation] (Examples 23~39)

To 100 g of the polyol thus obtained in the examples and comparative examples, 1.5 g of water, 1.5 g of silicone surfactant L-5420 (a product of Nippon Unicar Co., Ltd.), amine catalyst Kaolizer No. 1 (a product of Kao Co., Ltd.) and each amount of CFC or HCFC illustrated in Table 17 and 18 were added and mixed to obtain a premix. The premix thus obtained was mixed and reacted with each amount of polyisocyanate (MDI-CR, crude diphenylmethane diisocyanate, a product of Mitsui Toatsu Chemicals, Inc.) illustrated in the same table at the room temperature and poured into a mold to prepare a rigid polyurethane foam.

In the step of preparing the resin premix, mixing and dispersing ability (operation efficiency) between CFC or HCFC and polyol was observed and closed cell content of rigid polyurethane foam were measured. Results are illustrated in the same table.

As seen in Table 17 and 18, polyol(D), polyol(E) and polyol (G) which are respectively a mixture of phenol resin base polyol (A) and aminophenol base polyol (B) or polyphenylpolyxylylenepolyamine base polyol (C) or polymethylolphenylpolyamine base polyol (F) can maintain, in the polyurethane foam production using HCFC or HFC as a foaming agent, equivalent or better operation efficiency and foam properties as compared with conventional foam production using CFC.

Table 16 Polyurethane Resin

Example No.	12	13	14	15	16	17	18	19	20	21	22
Polyol No.	D-1	D-2	D-3	D-4	D-5	E-1	E-2	E-3	E-4	E-5	E-6
Formulation (g)											
Polyol (D) or (E)	30	30	30	30	30	30	30	30	30	30	30
MDI-CR	15.1	23.0	30.1	23.3	35.2	17.4	26.6	41.4	31.9	38.4	32.3
Kaolizer No. 1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Absorption (%)											
CFC-11(24hr)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
HFC-123(24hr)	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.1	0.0	0.0	0.0
HFC-141b(24hr)	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0

Note:

MDI-CR: Crude diphenylmethanediisocyanate a product of MITSUBI TOYOTSU CHEMICALS, INC.

Kaolizer No. 1: Amine base catalyst, a product of Kao Corp.

Absorption: Weight increase rate of a specimen of polyurethane resin having dimensions of 40X40X7~17mm after immersion in 50 g of fluid.

Table 17 Operation Efficiency in Foam Preparation and Closed Cell Content in Foam

Reference Example No.	23	24	25	26	27	28	29	30	31	32	33
Polyol No.	D-1	D-2	D-3	D-4	D-5	E-1	E-2	E-3	E-4	E-5	E-6
OH-value (mgOH/g)	210	320	420	325	486	243	370	577	445	535	450
Viscosity (cP/25 °C)	1300	8800	14000	7000	12000	20000	10200	5800	8200	12500	15800
Formulation (g)											
Polyol	100	—	—	—	—	—	—	—	—	—	—
H <sub>2</sub> O	1.5	—	—	—	—	—	—	—	—	—	—
L-5420	1.5	—	—	—	—	—	—	—	—	—	—
Emulsifier No. 1	1.2	1.2	0.8	0.8	0.8	1.2	1.2	0.8	1.2	0.8	2.0
Foaming agent	27.0	31.3	35.3	31.5	38.0	28.3	83.3	40.8	86.3	39.8	38.4
MDI-CL	79.9	108.8	135.1	110.0	153.5	88.5	122.0	170.6	141.7	165.4	143.0
Operation efficiency	all good										
CFC-11(24hr)											
HCFC-123(24hr)											
HCFC-141b (24hr)											
Closed cell content (%)											
CFC-11(24hr)	87.5	88.0	88.5	88.2	88.3	87.9	88.1	88.5	88.3	88.5	88.2
HCFC-123(24hr)	85.3	88.0	88.0	88.5	85.2	86.3	85.3	88.2	85.3	84.1	86.5
HCFC-141b (24hr)	87.5	88.2	87.3	88.3	85.4	88.3	88.5	88.6	85.3	88.2	88.2

Note: L-5420: Silicon surfactant (a product of Nippon Unica Co. Ltd.)

Closed cell content: Beckmann air comparison hydrometer (a product of Toshiba Beckmann Comp.)

Foaming agent: 3 foaming tests using CFC-11, HCFC-123 and HCFC-141b were carried out respectively according to the formulation in Table 17. Same amount of foaming agent was used. Operation efficiency and closed cell content of foams obtained were measured respectively. Table 18 is the same as Table 17.

Table 18 Operation Efficiency in Foam Preparation and Closed Cell Content in Foam

Reference Example No.	34	35	36	37	38	39
Polyol No.	G-1	G-2	G-3	G-4	G-5	G-6
OH-value (mgOH/g)	262	385	190	475	685	310
Viscosity (CP/25 °C)	18000	13100	14000	21000	22500	12500
Formulation (g)						
Polyol	100	→	→	→	→	→
H <sub>2</sub> O	1.5	→	→	→	→	→
I-5020	1.5	→	→	→	→	→
Isolizer No.1	1.5	1.5	1.5	1.5	0.8	1.2
Feeling agent	29.0	34.3	26.2	37.4	45.7	30.8
MDI-Q8	83.5	123.5	74.6	148.6	204.8	103.2
Operation efficiency	all good					
CFC-11(24hr)						
HCFC-123(24hr)						
HCFC-141b (24hr)						
Closed Cell Content (%)						
CFC-11(24hr)	88.5	88.3	89.0	88.0	88.5	90.1
HCFC-123(24hr)	86.5	87.5	88.0	88.0	87.0	88.5
HCFC-141b (24hr)	87.5	87.5	89.0	87.5	87.5	87.3

[Rigid polyurethane foam production] (continued) (Table 19~22)

Resin premix, was prepared according to the formulation illustrated in Tables 19~22. The premix was rapidly mixed at 5000 rpm for 6 seconds with a prescribed amount of an organic polyisocyanate as illustrated in above Tables. The mixture obtained was immediately poured into vertical, wooden boxes having dimensions of 200×200×200 mm and 380×380×35(thickness)mm.

The mixture was free foamed and thereafter allowed to stand for a day at room temperature.

Specimens having dimensions of 80×80×30mm in size were cut from the former mold and density, compressive strength, and low temperature dimensional stability were measured in accordance with JIS A 9514.

A specimens having dimensionds of 200×200×25mm in size were cut from the latter mold and heat conductivity were measured in accordance with JIS A 1412.

Results are illustrated in Tables 19~22.

#### (1) Preparation of rigid polyurethane foam composite having facing material

According to the above examples, preparation of a rigid polyurethane foam composite having facing material of the invention was carried out.

Polyols obtained in examples and comparative examples illustrated in Table 11 and Table 23 were used as the raw material of rigid polyurethane foams.



Table 20 Foam Property (Example 54~57, Comparative Example 8~14)

	Com. Ex		Example		Com. Ex		Example		Com. Ex		Example		Com. Ex		Example		Com. Ex		Example		Com. Ex		Example	
	8	54	55	9	56	57	10	58	59	11	60	61	12	62	63	13	64	65	14	66	67			
Raw material (g)																								
MDI - CR		88.5		122.0				170.8			141.7			165.4			141.7			141.7				
Polyol E-1		100																						
Polyol E-2				100																				
Polyol E-3								100																
Polyol E-4											100						100			100				
Polyol E-5													100											
H <sub>2</sub> O		1.5		1.5				1.5			1.5			1.5			1.5			1.5				
L - 5420		1.5		1.5				1.5			1.5			1.5			1.5			1.5				
Kaolizer No. 1		1.2		1.2				0.8			1.2			0.8			1.2			1.2				
Foaming agent																								
CFC-11	28			33			41			36			40			36			36					
HFC-141b		25			28			35			31			35			31			31				
HFC-123			34			40			49			44			48			40		40				
HFC-134a																		5						
Isopentane																						5		
Foam properties																								
Density ( kg/m <sup>3</sup> )	24.3	24.1	24.8	24.5	24.2	24.5	24.6	24.4	24.8	24.2	24.0	24.5	24.5	24.2	24.0	24.2	24.0	24.0	24.2	24.0	24.0			
Compressive Strength (kg/cm <sup>2</sup> )	1.80	1.80	1.73	1.75	1.70	1.70	1.75	1.74	1.74	1.73	1.77	1.74	1.79	1.75	1.77	1.75	1.77	1.70	1.75	1.77	1.77	1.71		
Low temperature dimensional stability (% -30 °C/24hr)	-0.3	-0.2	-0.3	0.0	-0.1	-0.3	-0.2	-0.1	-0.4	-0.1	-0.1	-0.2	-0.1	0.0	-0.3	-0.1	-0.1	-0.3	-0.1	-0.1	-0.1	-0.3		
Heat conductivity (kcal/m·hr·°C)	0.0160	0.0163	0.0164	0.0160	0.0162	0.0165	0.0162	0.0163	0.0165	0.0165	0.0166	0.0166	0.0168	0.0159	0.0162	0.0165	0.0166	0.0169	0.0165	0.0166	0.0169	0.0169		

Table 21. Foam Property (Example 63 ~81, Comparative Example 15~21)

	Com. Ex.	Example	Com. Ex.	Example	Com. Ex.	Examp.	Com. Ex.	Example	Com. Ex.	Example	Com. Ex.	Example	Com. Ex.	Example	Com. Ex.	Example	Com. Ex.	Example	Com. Ex.	Example	Com. Ex.	Example
	15	63	69	70	71	17	72	73	18	74	75	19	76	77	20	78	79	21	80	81		
Base material (g)																						
MDI 1-CR		93.5		128.5		74.6				149.6		204.8				149.6				149.6		
Polyol G-1		100																				
Polyol G-2				100																		
Polyol G-3						100																
Polyol G-4										100						100				100		
Polyol G-5													100									
H <sub>2</sub> O		1.5		1.5		1.5				1.5		1.5			1.5					1.5		
L-5420		1.5		1.5		1.5				1.5		1.5			1.5					1.5		
Emulsifier No. 1		1.5		1.5		1.5				1.5		0.8			1.5					1.5		
Foaming agent																						
CFE-11	29			34		26			37			31			37			37				
HFC-141b		25		30			23			32			27			32				32		
HFC-123			35		41			31			45			37			40			40		
HFC-134a																	5					
Isopentane																						5
Foam properties																						
Density (kg/m <sup>3</sup> )	24.6	24.7	25.2	24.8	25.0	24.4	24.5	25.5	25.0	25.1	25.8	25.5	25.9	25.0	25.0	25.1	25.0	25.0	25.1	25.2		
Compressive Strength (kg/cm <sup>2</sup> )	1.50	1.25	1.19	1.30	1.20	1.15	1.30	1.25	1.50	1.30	1.25	1.62	1.65	1.63	1.50	1.30	1.24	1.50	1.30	1.25		
Low temperature dimensional stability (K -30 °C/24hr)	-0.2	-0.8	-1.0	-0.6	-0.7	-1.0	-0.4	-1.0	-0.2	-0.6	-0.6	-0.2	-0.8	-1.4	-0.2	-0.6	-0.7	-0.2	-0.6	-0.8		
Heat conductivity (W/m·°C)	0.0165	0.0168	0.0170	0.0168	0.0170	0.0172	0.0165	0.0167	0.0163	0.0166	0.0166	0.0159	0.0163	0.0161	0.0163	0.0166	0.0159	0.0163	0.0166	0.0169		



Table 23

Polyol No.	R-1	R-2
Polyhydric alcohol	glycerol	glycerol, sucrose
Alkyrene oxide	propylene oxide	propylene oxide
Hydroxyl value (mgOH/g)	450	450
Viscosity (cp/25°C)	480	8500

Table 22 Foam Property (Comparative Example 22 ~27)

	Comparative Example					
	22	23	24	25	26	27
Raw material (g)						
MDI-62		1.44			1.44	
Polyol R-1		1.00				
Polyol R-2					1.00	
H <sub>2</sub> O		1.5			1.5	
L-5420		1.5			1.5	
Emulsifier No. 1		3.0			3.0	
Foaming agent						
CTC-11	3.7			3.7		
HFC-141b		3.0			3.0	
HFC-123			4.4			4.4
Foam properties						
Density (kg/m <sup>3</sup> )	24.5	25.1	25.2	25.0	25.2	25.3
Compressive Strength (kg/cm <sup>2</sup> )	1.51	0.97	1.01	1.61	0.98	0.95
Low temperature dimensional stability (% -30 °C/24hr)	-0.5	-3.6	-5.8	-1.0	-4.5	-7.5
Heat conductivity (kcal/mhr °C)	0.0170	0.0180	0.0185	0.0165	0.0180	0.0182

The facing material for use in the invention includes corrugated paper boards, laminated papers and other paper products, polyethylene, polypropylene, polyvinyl chloride and other synthetic resin plates; and aluminum, steel and other metal plates.

#### 1) Polyurethane foam composite having one facing material (Table 24, 25)

The same formulations as illustrated in Table 24 were sprayed on a facing material under the following conditions to prepare a rigid polyurethane foam having one facing material. Properties of the product obtained are summarized in Table 25.

Atomizer : Model - FF Head D Gum (a product of Gusmer Co., Ltd.)  
 Output pressure : 50 kg/cm<sup>2</sup>  
 Liquid temperature : 40 °C  
 Face material : Corrugated paper board

## 2) Preparation of rigid polyurethane foam having a plurality of facing material (Table 26, 27)

In the test, rigid polyurethane foam composite boards having two facing materials were prepared with a continuous process under the following conditions by using the formulations illustrated in Table 26.

5 Properties of the product obtained are summarized in Table 27.

Foaming machine : High pressure foam dispensing machine Model-MQ. (a product of Hennecke Maschinen Bau)

Line Speed : 10 m/min

Temperature : Material: 30 - 40 °C Cure oven: 55 °C

10 Product : 1 m Width x 40 mm Thickness 35 mm Foam layer

Facing material : Laminated paper on the top and bottom

As seen in these results, the polyols of the invention have suitable reactivity. Consequently, the mixture of foaming ingredients does not cause sagging phenomenon, even when it is sprayed on a vertical face material, and can give good appearance on the surface of spray applied foam. Good adhesion of sprayed foam to the face material can also be obtained. The rigid foam thus obtained has excellent flame retardance and low heat conductivity, and thus provides composite boards having excellent performance.

The formulations used in the preparation of rigid polyurethane foam composites are illustrated in Table 24 and 25. However, the formulations are not limited to the above embodiment and it is to be understood that the formulations illustrated in Table 11 and Table 18 (polyol D, E and G) can also be used for the preparation of polyurethane foam composites.

Table 24

Formulation (g)	Example			Comparative Example		
	82	83	84	28	29	30
MDI-CR	145.3	145.3	133.5	127	127	127
Polyol	100	100	100	100	100	100
D-5						
E-4						
R-1						
R-2						
TCEP	10	10	10	10	10	10
H <sub>2</sub> O	0.5	0.5	0.5	0.5	0.5	0.5
L-5420	1.5	1.5	1.5	1.5	1.5	1.5
Kaolizer No. 1	2.4	2.4	3.6	5.0	5.0	5.0
LL-680D	0.1	0.1	0.1	0.1	0.1	0.1
CFC-11						
HCFC-141b						
HCFC-123	32	44	42	19	17	23

Note: TCEP : Flame retardant, Tris (2-chloroethyl) phosphate  
a product of Daihachi Chem. Co.  
LL-680D: Catalyst, Lead octoate of 40% by weight  
dioctylphthalate solution

Table 25

	Example			Comparative Example		
	82	83	84	C. Ex.	Ex.	Ex.
Formulation (in Tabel 24)	Ex. 82	Ex. 83	Ex. 84	C. Ex. 29	Ex. 29	C. Ex. 30
Reactivity	4~5	4~5	4~5	5	5~6	5
Tack-free time (sec.)	none	none	none	none	exist	exist
Sag phenomenon (1)	good	good	good	good	good	good
Surface appearance	good	good	good	good	good	good
Adhesion	good	good	good	good	good	good
Foam density (kg/m <sup>3</sup> )	38.4	38.8	38.8	38.0	38.0	39.0
Compressive strength (kg/cm <sup>2</sup> )	3.34	3.35	3.30	3.25	3.10	2.95
Heat conductivity (kcal/mhr °C)	0.0165	0.0167	0.0170	0.0180	0.0190	0.0188
Combustibility (2)						
Combustion time (sec.)	22	20	21	24	35	33
Burned distance (mm)	18	17	19	19	20	21

Note: (1) Sag is a phenomenon where a raw material mixture before curing sags or runs down on a vertical surface when the mixture is sprayed to foam on the surface.

(2) Combustibility (Flame retardation): ASTM D 1691

(3) In formulation, Ex. indicates Example No. C. Ex. indicates Comparative Example No.

Table 26

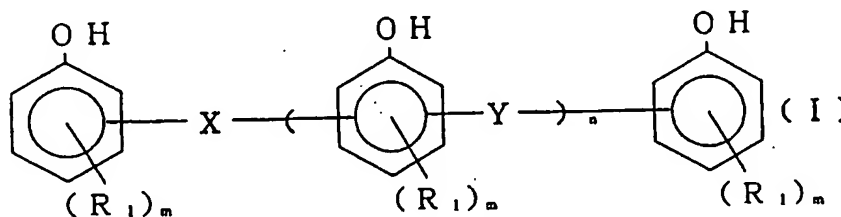
Formulation (g)	Example			Comparative Example		
	85	86	87	91	92	93
MDI-CR	135	135	143	144	144	144
Polyol	100	100	100	100	100	100
D-3						
E-6						
R-1						
R-2						
TCEP	10	10	10	10	10	10
H <sub>2</sub> O	1.5	1.5	1.5	1.5	1.5	1.5
L-5420	1.5	1.5	1.5	1.5	1.5	1.5
Kaolizer No. 1	0.8	0.8	2.0	3.0	3.0	2.8
CFC-11				37		
HCFC-141b					30	
HCFC-123	32	42	43			44

Table 27

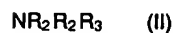
	Example	Comparative Example		
		31	32	33
Formulation (in Table 26)	85	87	87	87
Adhesion between face material and foam	good	good	good	good
Foam density (kg/m <sup>3</sup> )	30.3	31.0	31.0	31.5
Compressive strength (kg/cm <sup>2</sup> )	1.64	1.60	1.55	1.00
Flexural strength (kg/cm <sup>2</sup> )	2.50	2.44	2.45	1.85
Heat conductivity (kcal/mhr °C)	0.0163	0.0170	0.0170	0.0186
Combustibility				
Combustion time (sec.)	22	21	30	31
Combustion distance (mm)	16	15	21	20

## Claims

1. Polyol(D) comprising phenol resin base polyol(A) and aminophenol base polyol(B) in a ratio (A)/(B) of from 0.25 to 4.0 by weight and having a hydroxyl value of from 180 to 700 mgKOH/g.
2. The polyol(D) of claim 1 wherein the phenol resin base polyol(A) comprises polyol(a) and polyol(b), or polyol (a) and polyol (c):  
polyol(a) having a hydroxyl value of from 140 to 350 mgKOH/g and being prepared by the addition of from 1.0 to 4.5 moles of an alkylene oxide to one equivalent of hydroxyl of a phenol resin or a mixture hereof having a number average molecular weight of from 650 to 1400, an average functionality of from 3 to 8 and the formula (I):

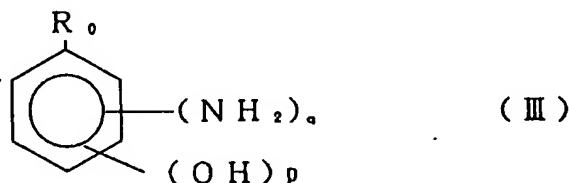


wherein  $\text{R}_1$  is a hydrogen atom, alkyl having from 1 to 9 carbon atoms, halogen atom selected from chlorine, bromine and fluorine, or hydroxyl,  $m$  is an integer of from 1 to 3,  $n$  is an integer of from 1 to 6, and  $X$  and  $Y$  are same or different divalent groups selected from the group consisting of an alkylene having from 1 to 10 carbon atoms, xylylene, oxy, thio and sulfonyl or bonded group of the above-mentioned groups; said polyol(b) having a hydroxyl value of 240 to 800 mgKOH/g and being obtained by adding from 0.5 to 3.0 moles of an alkylene oxide to one equivalent of active hydrogen in an alkanolamine series compound or a mixture thereof having the formula (II):



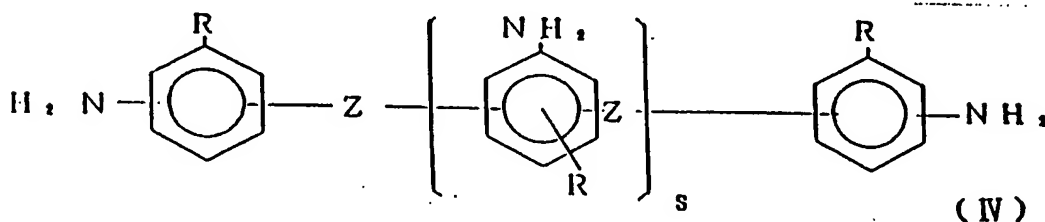
wherein  $R_2$  and  $R_3$  are respectively a hydrogen atom, hydroxyethyl or hydroxyisopropyl,  $R_2$  and  $R_3$  are same or different and excluding the case wherein both  $R_2$  and  $R_3$  are hydrogen atoms; said polyol(c) having a hydroxyl value of 130 to 750 mgKOH/g and being obtained by the addition of from 0.8 to 6.5 moles of an alkylene oxide to one equivalent of hydroxyl group in an active hydrogen containing compound which is an aliphatic polyhydroxy compound having average functionality of from 2 to 8 or a mixture thereof.

3. The polyol(D) of claim 2 wherein the phenol resin is a novolak resin represented by the formula (I) wherein  $R_1$  is a hydrogen atom and both X and Y are methylene.
4. The polyol(D) of claim 3 wherein the novolak resin has a number average molecular weight of from 650 to 900, average functionality of from 3 to 8, and a softening point of from 75 to 120 °C.
5. The polyol(D) of claim 1 wherein the aminophenol base polyol(B) comprises polyol(d) having a hydroxyl value of from 150 to 700 mgKOH/g and polyol(b) or polyol(c) of claim 2, said polyol(d) being obtained by adding from 1.0 to 9.0 moles of an alkylene oxide to one equivalent of active hydrogen in an aminophenol series compound or a mixture thereof having a number average molecular weight of from 100 to 200, average functionality of from 3 to 6, and the formula (III):



wherein  $R_0$  is a hydrogen atom, aliphatic hydrocarbon group having from 1 to 5 carbon atoms, or alicyclic hydrocarbon group, q is an integer of from 1 to 2, and p is an integer of from 1 to 2.

6. The polyol(D) of claim 2 wherein the phenol resin base polyol(A) has a polyol(a)/polyol(b) ratio of from 0.25 to 4.0 by weight and a polyol(a)/polyol(c) ratio of from 0.1 to 4.0 by weight.
7. The polyol(D) of claim 5 wherein the aminophenol base polyol(B) has a polyol(d)/polyol(b) ratio of from 0.25 to 4.0 by weight and a polyol(d)/polyol(c) ratio of from 0.1 to 4.0 by weight.
8. Polyol(E) comprising the phenol resin base polyol(A) of claim 2 and a polyphenylpolyxylylenepolyamine base polyol(C) in a (A)/(C) ratio of from 0.25 to 4.0 by weight, said polyol(E) having a hydroxyl value of from 180 to 700 mgKOH/g.
9. The polyol(E) of claim 8 wherein the polyphenylpolyxylylenepolyamine base polyol(C) comprises a polyol(e) having a hydroxyl value of from 150 to 700 mgKOH/g and polyol(b) or polyol(c) of claim 2, said polyol(e) being obtained by adding from 1.0 to 9.0 moles of an alkylene oxide to one equivalent of active hydrogen in a polyphenylpolyxylylenepolyamine series compound or a mixture thereof having a number average molecular weight of from 300 to 1500, average functionality of from 4 to 8 and the formula (IV):



wherein R is a hydrogen atom, aliphatic hydrocarbon having from 1 to 10 carbon atoms, or an alicyclic hydrocarbon, Z is xylylene and s is an integer of from 0 to 10.

10. Polyol(E) of claim 8 wherein the polyphenylpolyxylenepolyamine base polyol(C) has a polyol(e)-/polyol(b) ratio of from 0.25 to 4.0 by weight and a polyol(e)/polyol(c) ratio of from 0.1 to 4.0 by weight.
11. A polyurethane resin obtained by the reaction of a polyol with an organic polyisocyanate, a portion or the whole of said polyol comprising the polyol(D) of claim 1.
12. A polyurethane resin obtained by the reaction of polyol with an organic polyisocyanate, a portion or the whole of said polyol comprising the polyol (E) of claim 8.
13. The polyurethane resin of claim 11 or 12 wherein the organic polyisocyanate comprises an isocyanate terminated prepolymer.
14. The polyurethane resin of claim 11 or 12 wherein the equivalent ratio of an isocyanate group in the organic polyisocyanate to a hydroxyl group in the polyol is in the range of from 0.8 to 5.0.
15. A rigid polyurethane foam obtained by the reaction of an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator, other additives and optionally an auxiliary foaming agent, said polyol comprising a portion or the whole of polyol(D) of claim 1, said foaming agent comprising a single compound or a mixture thereof selected from the group consisting of a hydrochlorofluorocarbon or a hydrofluorocarbon.
16. A rigid polyurethane foam obtained by the reaction of an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator, other additives and optionally an auxiliary foaming agent, said polyol comprising a portion or the whole of polyol (E) of claim 8, said foaming agent comprising a single compound or a mixture thereof selected from the group consisting of a hydrochlorofluorocarbon or a hydrofluorocarbon.
17. The rigid polyurethane foam of claim 15 or 16 wherein the hydrochlorofluorocarbon is 2,2-dichloro-1,1,1-trifluoroethane, 1,1-dichloro-1-fluoroethane or 1-chloro-1,1-difluoromethane, and the hydrofluorocarbon is 1,1,1,2-tetrafluoroethane or 1,1-difluoroethane.
18. The rigid polyurethane foam of claim 15 or 16 wherein the foaming agent is water and/or a low boiling point compound.
19. The rigid polyurethane foam of claim 15 or 16 wherein the organic polyisocyanate comprises an isocyanate terminated prepolymer.
20. The rigid polyurethane foam of claim 15 or 16 wherein the equivalent ratio of an isocyanate group in the organic polyisocyanate to a hydroxyl group in the polyol is in the range of from 0.8 to 5.0.
21. A preparation process of a rigid polyurethane foam by reacting an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator other additives and optionally an auxiliary foaming agent, said polyol comprising a portion or the whole of polyol(D) of claim 1, said foaming agent comprising a single compound or a mixture thereof selected from the group consisting of a hydrochlorofluorocarbon or a hydrofluorocarbon.
22. A preparation process of a rigid polyurethane foam by reacting an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator other additives and optionally an auxiliary foaming agent, said polyol comprising a portion or the whole of polyol (E) of claim 8, said foaming agent comprising a single compound or a mixture thereof selected from the group consisting of a hydrochlorofluorocarbon or a hydrofluorocarbon.
23. The preparation process of claim 21 or 22 wherein a portion or the whole of the organic polyisocyanate comprises an isocyanate terminated prepolymer.

24. The preparation process of claim 21 or 22 wherein the equivalent ratio of an isocyanate group in the organic polyisocyanate to a hydroxyl group in the polyol is in the range of from 0.8 to 5.0.
- 5 25. A preparation process of a rigid polyurethane foam composite by reacting an organic polyisocyanate with a premix comprising a polyol, foaming agent, catalyst, cell regulator, other additives and optionally an auxiliary foaming agent to form a rigid polyurethane foam on a face material or in a cavity surrounded by a plurality of face material, said polyol comprising a portion or the whole of polyol(D) of claim 1, said foaming agent comprising a single compound or a mixture thereof select from the group consisting of a hydrochlorofluorocarbon and a hydrofluorocarbon.
- 10 26. A preparation process of a rigid polyurethane foam composite by reacting an organic polyisocyanate with a premix comprising a polyol, foaming agent, catalyst, cell regulator, other additives and optionally an auxiliary foaming agent to form a rigid polyurethane foam on a face material or in a cavity surrounded by a plurality of face material, said polyol comprising a portion or the whole of polyol (E) of claim 8, said foaming agent comprising a single compound or a mixture thereof select from the group consisting of a hydrochlorofluorocarbon and a hydrofluorocarbon.
- 15 27. The preparation process of claim 25 or 26 wherein the rigid polyurethane foam is formed by a coating, pouring or spraying process.
- 20 28. The preparation process of claim 25 or 26 wherein a portion or the whole of the organic polyisocyanate comprises an isocyanate terminated prepolymer.
- 25 29. The preparation process of claim 25 or 26 wherein the equivalent ratio of an isocyanate group in the organic polyisocyanate to a hydroxyl group in the polyol is in the range of from 0.8 to 5.0.
- 30 30. A rigid polyurethane foam obtained by reacting an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator, other additives and optionally an auxiliary foaming agent, said polyol comprising a portion or the whole of polyol (G) having a hydroxyl value of from 180 to 700 mgKOH/g and containing phenol resin base polyol(A) of claim 2 and polymethylenepolyphenylpolyamine base polyol(F) in a (A)/(F) ratio of from 0.25 to 4.0 by weight, said foaming agent comprising a compound or a mixture thereof selected from the group consisting of a hydrochlorofluorocarbon and a hydrofluorocarbon.
- 35 31. The rigid polyurethane foam of claim 30 wherein the polymethylenepolyphenylpolyamine base polyol(F) comprises polyol(f) having a hydroxyl value of from 150 to 700 mgKOH/g and polyol(b) or polyol(c) of claim 2, said polyol(f) being obtained by the addition of from 1.0 to 9.0 moles of an alkylene oxide to one equivalent of active hydrogen in polymethylenepolyphenylpolyamine.
- 40 32. The rigid polyurethane foam of claim 30 wherein a portion or the whole of the organic polyisocyanate comprises an isocyanate terminated prepolymer.
- 45 33. The rigid polyurethane foam of claim 30 wherein the equivalent ratio of an isocyanate group in the organic polyisocyanate to a hydroxyl group of the polyol is in the range of from 0.8 to 5.0.
- 50 34. A preparation process of rigid polyurethane foam by the reaction of an organic polyisocyanate with a resin premix comprising polyol, foaming agent, catalyst, cell regulator, other additives and optionally an auxiliary foaming agent, said polyol comprising a portion or the whole of polyol(G) having a hydroxyl value of from 180 to 700 mgKOH/g and containing phenol resin base polyol(A) of claim 2 and polymethylenepolyphenylpolyamine base polyol(F) of claim 31 in a (A)/(F) ratio of from 0.25 to 4.0 by weight, said foaming agent comprising a compound or a mixture thereof selected from the group consisting of a hydrochlorofluorocarbon and a hydrofluorocarbon.
- 55 35. The preparation process of claim 34 wherein a portion or the whole of the organic polyisocyanate comprises an isocyanate terminated prepolymer.
36. The preparation process of claim 34 wherein the equivalent ratio of an isocyanate group in the organic polyisocyanate to a hydroxyl group in the polyol is in the range of from 0.8 to 5.0.

37. A preparation process of a rigid polyurethane foam composite by the reaction of an organic polyisocyanate with a resin premix comprising a polyol, foaming agent, catalyst, cell regulator, other additives and optionally an auxiliary foaming agent to form rigid polyurethane foam on a face material or in a cavity surrounded by a plurality of face material, said polyol comprising a portion or the whole of polyol(G) having a hydroxyl value of from 180 to 700 mgKOH/g and containing phenol resin base polyol(A) of claim 2 and polymethylenepolyphenylpolyamine base polyol(F) of claim 26 in a (A)/(F) ratio of from 0.25 to 4.0 by weight, said foaming agent comprising a compound or a mixture thereof selected from the group consisting of a hydrochlorofluorocarbon and a hydrofluorocarbon.
38. The preparation process of claim 37 wherein a portion or the whole of the organic polyisocyanate comprises an isocyanate terminated prepolymer.
39. The preparation process of claim 37 wherein the equivalent ratio of an isocyanate group in the organic polyisocyanate to a hydroxyl group in the polyol is in the range of from 0.8 to 5.0.
40. The preparation process of claim 37 wherein the rigid polyurethane foam is formed by coating, pouring or spraying.





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# EUROPEAN SEARCH REPORT

Application Number

EP 90 31 2063

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL5)
A	FR-A-2223416 (DOW CHEMICAL) * page 1, line 20 - page 3, line 16; claims 1-6 *	1-4	C08G18/54 C08G18/40
A	--- CHEMICAL ABSTRACTS, vol. 101, no. 12, September 1984 Columbus, Ohio, USA "Thermally stable polyurethane resins" page 40; column 2; ref. no. 92044X * abstract *	1, 8	
A	--- CHEMICAL ABSTRACTS, vol. 104, no. 6, February 1986 Columbus, Ohio, USA Asano et al.: "Polyol compositions for rigid polyurethane foams" page 38; column 1; ref. no. 34863Q * abstract *	1	
A	--- GB-A-934629 (DISTILLERS) * page 1, line 17 - page 2, line 11; claims 1-7 *	1	TECHNICAL FIELDS SEARCHED (Int. CL5)
A	--- US-A-3499009 (ODINAK ET AL.) * column 2, line 1 - column 7, line 47; claims 1-8 *	1, 8	C08G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 JUNE 1991	Examiner BOURGONJE A. F.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	